UNCONTROLLED COPY

Controlled Copy
Copy No:_____

SOP No: CORP-OP-0001
Revision No: 2
Revision Date: 01/31/96
Page 1 of 90

QUANTERRA STANDARD OPERATING PROCEDURE

TITLE: **EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATERS AND SOILS, BASED ON SW-846 3500 SERIES, 3600 SERIES, 8150, 8151 AND 600 SERIES METHODS.**

(SUPERSEDES: Revision 1)

Prepared by: Richard Burrows

Reviewed by: _____
Technology Standardization Committee

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Health and Safety

Approved by: _____
Management

Proprietary Information Statement:

This document has been prepared by and remains the sole property of Quanterra Inc. It is submitted to a client or government agency solely for its use in evaluating Quanterra's qualifications in connection with the particular project, certification, or approval for which it was prepared and is to be held proprietary to Quanterra.

The user agrees by its acceptance or use of this document to return it upon Quanterra's request and not to reproduce, copy, lend or otherwise dispose or disclose of the contents, directly or indirectly, and not to use it for any purpose other than that for which it was specifically furnished. The user also agrees that where consultants or others outside of the user's organization are involved in the evaluation process, access to these documents shall not be given to those parties unless those parties also specifically agree to these conditions.

TABLE OF CONTENTS

List of Appendices:

List of Tables

1. SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8150A.

2. SUMMARY OF METHOD

This method is based on SW846 method 8150A. Aqueous samples are extracted into diethyl ether by a separatory funnel extraction. Solids are extracted into diethyl ether by shaking. Phenoxy acid herbicides in the extract are hydrolyzed with potassium hydroxide and the aqueous solution is washed with diethyl ether to remove interferences. The aqueous solution is then acidified and the herbicides are extracted with diethyl ether. The ether solution is dried and the herbicides are esterified using diazomethane. The final volume is adjusted to prepare the extract for gas chromatography.

3. DEFINITIONS

Refer to section 3 of the main body of this SOP.

4. *INTERFERENCES*

Refer to section 4 of the main body of this SOP.

5. SAFETY

5.1. Refer to section 5 of the main body this SOP for basic safety information.

5.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

5.3. Diethyl ether is extremely flammable

5.4. Diethyl ether must be free of peroxides as demonstrated by EM Quant test strips.

5.5. Concentrated potassium hydroxide solution is highly caustic.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

6.2. Diazomethane generation apparatus

6.3. EM Peroxide test strips

7. REAGENTS AND STANDARDS

7.1. Reagents are listed in Section 7 of the main body of this SOP. Additional Reagents and standards needed for this procedure are listed below.

7.2. Reagents

7.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. CAUTION: Considerable heat will be generated.

7.2.2. Diazald, 99% purity

7.2.3. Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 1000 g sodium sulfate with just enough diethyl ether to cover. Add 2-5 mL of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

7.2.4. Acidified 5% sodium sulfate solution

Add 50 g of sodium sulfate to one liter of reagent water. Add 10 mL of concentrated H_2SO_4. (This reagent may be prepared in different quantities if the proportions are kept the same).

7.2.5. Diethyl ether, reagent grade.

7.2.6. Methanol, reagent grade.

7.2.7. Silicic acid

7.3. Standards

7.3.1. Surrogate Standard

See Table A3.

7.3.2. Matrix Spike and LCS standard

See Table A4.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

10. CALIBRATION AND STANDARDIZATION

Not applicable

11. PROCEDURE

11.1. Preparation of soil, sediment and other solid samples

11.1.1. Weigh 50.0 g of moist solid sample into an 8 oz. glass jar. Use 50 g of sodium sulfate for the Method Blank and LCS. Acidify the sample with 5 mL of concentrated HCl.

11.1.2. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

11.1.3. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS is not determined.)

11.1.4. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

11.1.5. Spike with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables A1 and A2)

11.1.6. Add 100 mL 20% acetone in ethyl ether.

Note: If dinoseb is a target, acetone should not be used. Instead, use 100 mL of ethyl ether.

11.1.7. Mix contents on orbital shaker for 20 minutes. Decant extract through glass wool plugged funnel.

11.1.8. Extract sample twice more, using 100 mL 20% acetone in ether (or 100% ether if dinoseb is a target). After each addition shake for 10 minutes and decant the extract.

11.1.9. Combine the extracts in a 1 or 2 liter separatory funnel containing 250 mL of acidified 5% sodium sulfate solution.

11.1.10. Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for one minute to extract interferences into the aqueous layer. Allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase in a 500 mL ground glass Erlenmeyer flask. Place the aqueous phase back in the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500 mL Erlenmeyer flask containing 5 mL of 37% potassium hydroxide. Proceed to step 11.3, Hydrolysis.

11.2. Preparation of Aqueous Samples

11.2.1. Weigh the sample bottle and pour approximately 1 liter (100 mL for TCLP leachates) into a 2 liter separatory funnel. The sample should be decanted off any sediment. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 1 liter in a graduated cylinder. If less than 1 liter was used, add reagent water to make the volume up to 1 liter.

11.2.2. Adjust pH to 2 with 1:1 sulfuric acid. Spike with 1 mL of surrogate solution. Spike MS/MSD and LCS samples with 1 mL of matrix spiking solution. (Refer to Tables A1 and A2). Add 150 mL diethyl ether and shake funnel for 2 minutes with frequent venting to release excess pressure. ***Caution:*** Diethyl ether will generate pressure rapidly. Vent the funnel immediately after it is first sealed and inverted, and vent frequently thereafter.

11.2.3. Allow layers to separate for at least 10 minutes and drain the aqueous phase into a clean beaker. If an emulsion forms break by centrifuge or mechanically. Collect the solvent extract (upper layer) in a 500 mL Erlenmeyer containing 2 mL of 37% potassium hydroxide. Use 5 mL of potassium hydroxide for TCLP samples.

11.2.4. Repeat the extraction two more times using 50 mL of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. Rinse the beaker with each additional aliquot of extraction solvent. Proceed to section 11.3, Hydrolysis.

11.3. Hydrolysis

11.3.1. Add one or two clean boiling chips, the sample extract, and 15 mL of water for water samples (30 mL for soil samples) to the 500 mL flask. Attach a three-ball Snyder column.

11.3.2. Place the apparatus on a hot water bath (approx 60°C) so that the bottom of the flask is bathed with hot water vapor. Although the diethyl ether will evaporate in about 15 minutes, continue heating for a total of 60 minutes), beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 minutes. Check the pH of the solution. If not at or above 11, add additional KOH to bring the pH above 11 and hydrolyze for an additional 60 minutes.

11.4. Solvent Clean-up

11.4.1. Transfer the solution to an acid-rinsed 125 or 250 mL separatory funnel using 5-10 mL of reagent water to rinse out the flask. Wash the basic solution by shaking for 1 minute with a 20 mL portion of diethyl ether. Drain the aqueous (bottom) layer back into the flask and discard the ether layer. Pour the aqueous layer back into the separatory funnel and repeat the wash with a second 20 mL of ether. Pour the aqueous phase back into the separatory funnel. The herbicides remain in the aqueous phase. Additional washes may be used if the sample appears dirty.

11.5. Solvent Extraction

11.5.1. Acidify the contents of the separatory funnel to pH 2 by adding 1:1 sulfuric acid (2 mL for aqueous, 5 mL for soils). Test with pH indicator paper. Add 40 mL ether and shake vigorously for 1 minute. Drain and collect the aqueous phase and pour the ether phase into a flask or bottle containing 5-7 g of acidified sodium sulfate.

11.5.2. Pour the aqueous phase back into the separatory funnel and repeat the extraction twice more with 20 mL aliquots of ether, combining all solvent in the flask or bottle. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours.

NOTE: The drying step is very critical to ensure complete esterfication. Any moisture remaining in the ether will result in low herbicide recoveries. The amount of sodium sulfate is adequate if some free flowing crystals are visible when swirling the flask. If all the sodium sulfate solidifies in a cake, add a few additional grams of sodium sulfate and again test by swirling. The 2 hour drying time is a minimum, however, the extracts may be held in contact with the sodium sulfate overnight.

11.6. Concentration

11.6.1. Transfer the ether extract by decanting, or through a funnel plugged with acid washed glass wool, into a Turbovap concentrator tube or a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the Erlenmeyer with 20-30 mL ether to complete transfer.

11.6.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2-5 mL, remove from the water bath and allow to completely cool.

11.6.3. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

11.6.4. Add 0.1 mL of methanol.

11.6.5. The extract is now ready for esterification by either the diazomethane solution method (11.7) or the bubbler method (11.8)

11.7. Esterification (diazomethane solution method)

11.7.1. Preparation of Diazomethane solution

- **CAUTION: Diazomethane is potentially explosive.**
- **A temporary shield or the sash of the hood must protect the face and body of the analyst.**
- **Never heat solutions of diazomethane above 90°C, due to the explosive potential.**
- **Do not use glass stirring rods or any glassware with ground glass joints, as this can initiate violent reaction or explosion.**
- **All glassware must be scrupulously cleaned and free from scratches, to avoid potential initiation of violent reaction or explosion.**

11.7.1.1. Weigh out 10.0 g potassium hydroxide in a 125 mL beaker. Add 16 mL water and 20 mL ethanol. Mix well until the potassium hydroxide is dissolved and pour into the reaction vessel.

11.7.1.2. Attach a 100 mL receiving flask to the condenser and cool the receiver in an ice bath.

11.7.1.3. Fill the condenser with dry ice, then add acetone slowly until the cold finger is about one third full.

11.7.1.4. Mix 10.0 g diazald and 90 mL ether. Place in a separatory funnel over the reaction vessel.

11.7.1.5. Warm the reaction vessel on the water bath to 50-60°C or until the ether begins to reflux. CAUTION: Do not allow the temperature to exceed 70°C. Add diazald solution over a period of 40 minutes. The rate of distillation should approximate the rate of addition. Replenish the cold finger with dry ice as necessary.

11.7.1.6. When the diazald solution has been used up, slowly add 10 mL of ether and continue distillation until the distillate is colorless.

11.7.1.7. The diazomethane solution is documented with a lot number. It is stored in a freezer at -10 to -20°C and has an expiration date of six months.

11.7.2. Disposal of outdated diazomethane solutions

11.7.2.1. Add 20 mL of ether to 2 mL of glacial acetic acid in a large beaker in the hood.

11.7.2.2. Add the diazomethane solution slowly to the acetic acid. The yellow color of the diazomethane disappears as it reacts with the acetic acid. If the yellow color persists at any time during the addition, and does not disappear with gentle swirling of the beaker, add additional acetic acid in ether before continuing the diazomethane addition.

11.7.2.3. Dispose of the ether solution in the non-chlorinated wastes bottle.

11.8. Esterification (Diazomethane solution method)

11.8.1. Add approximately 2 mL of diazomethane solution and let sit for 10-15 minutes.

11.8.2. Add approximately 0.2 g of silicic acid to the extract. Allow to spontaneously evaporate to about 1.0 mL, then make up to 10 mL with hexane.

11.8.3. Extract is ready for analysis by gas chromatography.

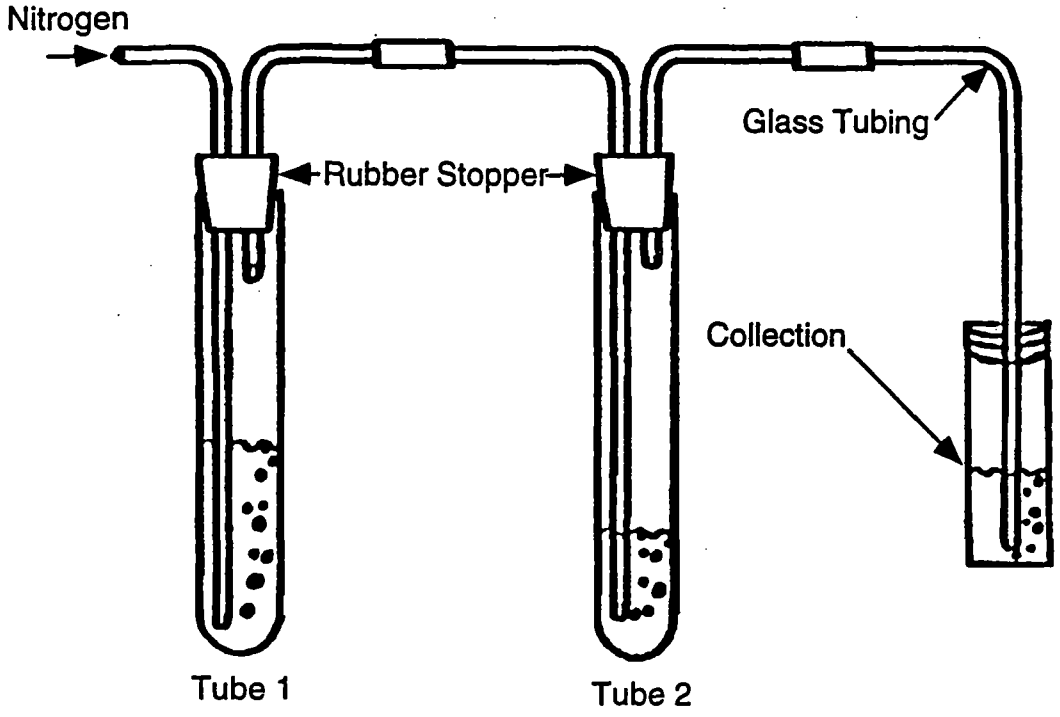
11.9. Esterification (Bubbler Method)

11.9.1. Assemble the diazomethane apparatus (Figure A1) in a hood. Add 10 mL of diethyl ether to tube 1. Add 5 mL of 2% methanolic KOH, 3 mL of ether and 0.5-1 g of diazald to tube 2.

11.9.2. Place the tip of the disposable pipet into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 1 minute, or until the yellow color persists. Replace the disposable pipet and place the tip into the vial containing the second extract. Continue until the diazald is consumed. (An additional 0.1-0.5 g diazald may be added to extend the generation of diazomethane).

11.9.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silicic acid to each extract. Allow to stand for an additional 20 minutes.

11.9.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.



12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

Refer to CORP-GC-0001 for details of method performance.

14. POLLUTION PREVENTION

Refer to section 14 of the main body of this SOP.

15. WASTE MANAGEMENT

Refer to section 15 of the main body of this SOP.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, September 1994, Chlorinated Herbicides, Method 8150B.

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.1.2)

17.1.2. Directions to add sodium sulfate to the soil sample until a free flowing texture is achieved have been added. In common with other SW-846 extraction procedures, this improves the extraction efficiency. (Section 11.1.4)

17.1.3. For the soil extraction, the acetone and ether are added together rather than separately. (Section 11.1.6)

17.1.4. The requirement for the sulfuric acid added in the solvent extraction to be cold has been removed. Since a small quantity of acid is added to a large quantity of extract, nothing is gained by having the acid cold. (Section 11.5.1)

17.1.5. Silicic acid is stored at room temperature.

17.1.6. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

17.2. Modifications from previous revisions

In the hydrolysis procedure, the extract is added to the potassium hydroxide solution rather than visa versa.

17.3. Tables

Table A1
Herbicide Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
Herbicides	Herbicides SS	1.0

Table A2
Herbicide Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
Herbicides	Herbicides MS	1.0

Table A3
Herbicide Surrogate Spike Components

Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides SS	2,4-DCAA	Methanol	16

[1]The surrogate is spiked as the free acid

Table A4			
Herbicide Matrix Spike Components			
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides MS	2,4-D	Methanol	16
	2,4-DB		16
	2,4,5-TP (Silvex)		4
	Dalapon		8
	2,4,5-T		4

[1]The herbicide spiking solution contains the herbicides as the free acids.

1. SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in CORP-GC-0001, Appendix D, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8151.

2. SUMMARY OF METHOD

This method is based on SW846 method 8151. Aqueous samples are hydrolyzed if esters and acids are to be determined, then washed with methylene chloride by a separatory funnel extraction. After acidifying the sample the free acids are extracted into diethyl ether. Solids are extracted into methylene chloride/ acetone by sonication. If esters and acids are to be determined, the extract is hydrolyzed and extracted into diethyl ether. For both soils and aqueous samples, the free acid herbicides in the ether extract are esterified. The final volume is adjusted to prepare the extract for gas chromatography.

3. DEFINITIONS

Refer to section 3 of the main body of this SOP.

4. INTERFERENCES

Refer to section 4 of the main body of this SOP.

5. SAFETY

5.1. Refer to section 5 of the main body this SOP for basic safety information.

5.2. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free of scratches, cracks, chips and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.

5.3. Diethyl ether is extremely flammable

5.4. Diethyl ether must be free of peroxides as demonstrated by EM Quant test strips.

5.5. Concentrated potassium hydroxide solution is highly caustic.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

6.2. Diazomethane generation apparatus

6.3. EM Peroxide test strips

7. REAGENTS AND STANDARDS

7.1. Reagents are listed in Section 7 of the main body of this SOP. Additional Reagents and standards needed for this procedure are listed below.

7.2. Reagents

7.2.1. Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

7.2.2. Sodium hydroxide solution, 6N. Dissolve 400 g NaOH in reagent water and dilute to 1.0L. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

7.2.3. Sodium hydroxide solution, 0.1N. Dissolve 4g NaOH in reagent water and dilute to 1.0L. Other volumes of solution may be made up as convenient.

7.2.4. Sulfuric acid, 1:1 Slowly add 500 mL concentrated sulfuric acid to 500 mL water. **Caution:** Considerable heat will be generated. The acid must be added to the water. Wear protective clothing and safety glasses. Other volumes of solution may be made up as convenient.

7.2.5. Diazald, 99% purity

7.2.6. 2,3,4,5,6-Pentafluorobenzyl bromide (PFBBr)$C_6H_5CH_2Br$

7.2.7. Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 1000 g sodium sulfate with just enough diethyl ether

to cover. Add 2-5 mL of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

7.2.8. Sodium Chloride, NaCl

7.2.9. Acidified 5% sodium sulfate solution

Add 50 g of sodium sulfate to one liter of reagent water. Add 10 mL of concentrated H_2SO_4. (This reagent may be prepared in different quantities if the proportions are kept the same).

7.2.10. Diethyl ether, reagent grade.

7.2.11. Methanol, reagent grade.

7.2.12. Silicic acid

7.3. Standards

7.3.1. Surrogate Standard

See Table A3.

7.3.2. Matrix Spike and LCS standard

See Table A4.

8. SAMPLE COLLECTION PRESERVATION AND STORAGE

8.1. Sample collection and storage is described in Section 8 of the main body of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the main body of this SOP for Quality control procedures.

10. CALIBRATION AND STANDARDIZATION

Not applicable

11. PROCEDURE

11.1. Preparation of Aqueous Samples

11.1.1. Weigh the sample bottle and pour approximately 1 liter (100 mL for TCLP leachates) into a 2 liter separatory funnel. Reweigh the bottle and record the sample volume on the benchsheet, assuming a density of 1.0. Alternatively, measure 1 liter in a graduated cylinder. If less than 1 liter was used, add reagent water to make the volume up to 1 liter.

11.1.2. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables B1 and B2)

11.1.3. Add 250 g of NaCl to the sample and shake to dissolve the salt.

11.1.4. Hydrolysis

Use this step only if herbicide esters in addition to herbicide esters are to be determined. This is normally the case. If the herbicide esters are not to be determined, omit this step and go to 11.1.4.

Add 17 mL of 6N NaOH to the sample, seal and shake. Check the pH of the sample with pH paper. If the pH of the sample is not $\geq$12 adjust to $\geq$12 by adding more NaOH. Let the sample sit at room temperature for 2 hours to complete the hydrolysis.

11.1.5. If the sample was originally in a 1 liter bottle, and the whole sample was used, add 60 mL of methylene chloride to the sample bottle. Rinse the bottle (and graduated cylinder, if used) and add the methylene chloride to the separatory funnel.

11.1.6. If the whole contents of the sample bottle were not used, add 60 mL of methylene chloride to the separatory funnel.

11.1.7. Extract the sample by shaking vigorously for 2 minutes. (An automatic shaker may be used). Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

11.1.8. Discard the **methylene chloride** phase.

11.1.9. Add a second 60 mL of methylene chloride and repeat the extraction a second time, discarding the methylene chloride. Repeat the extraction a third time.

11.1.10. Add 17 mL of cold (4°C) 1:1 sulfuric acid to the sample. Seal, and shake to mix. Check the pH of the sample with pH paper. If the pH is not ≤ 2, and more acid to adjust the pH to ≤ 2.

11.1.11. Add 120 mL diethyl ether to the sample and extract by shaking vigorously for 2 minutes. (An automatic shaker may be used). Allow the organic layer to separate from the aqueous layer. If a emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

11.1.12. Drain the aqueous layer into a clean flask or beaker. Collect the ether phase in a clean flask or bottle containing approximately 10g of acidified anhydrous sodium sulfate.

11.1.13. Return the aqueous phase to the separatory funnel, add 60 mL diethyl ether and repeat the extraction procedure a second time., combining the ether extracts. Repeat the extraction a third time with 60 mL diethyl ether. Discard the aqueous phase after the third extraction.

11.1.14. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken.

11.1.15. Proceed to section 11.5, concentration.

11.2. Extraction of soil and sediment samples

11.2.1. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator). Document if a water layer was discarded.

11.2.2. Weigh 50.0 g of moist solid sample into an clean glass jar. Use 50 g of sodium sulfate for the Method Blank and 50g Ottawa sand for the LCS. Acidify the sample with 5 mL of concentrated HCl.

11.2.3. There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

11.2.4. After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS are not determined.)

11.2.5. Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

11.2.6. Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to tables B1 and B2)

11.2.7. Add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker.

11.2.8. Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

11.2.9. Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn with mode switch on pulse, and percent-duty cycle knob set at 50%.

11.2.10. Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

11.2.11. Place the prepared funnel on a collection apparatus. If the herbicide esters are *not* to be determined, the collection apparatus is a bottle or flask containing approximately 10g of anhydrous acidified sodium sulfate. If the herbicide esters *are* to be determined, (normally the case) the collection apparatus is glassware suitable for the hydrolysis step, typically a KD flask or Turbovap tube.

11.2.12. Decant and filter extracts through the prepared funnel into the collection apparatus.

11.2.13. Repeat the extraction two more times with additional 100 mL minimum portions of methylene chloride / acetone each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

11.2.14. If the herbicide esters are not to be determined, dry the extract as described in 11.4.2 or go to cleanup, section 11.3. If the herbicide esters are to be determined (normally the case) proceed to section 11.2.15

11.2.15. Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Check the pH with pH paper. If the pH is not $\geq$12, adjust with additional KOH.

11.2.16. Heat on a water bath at 60-60°C for 2 hours. Allow to cool.

11.2.17. Transfer the solution to a separatory funnel and extract three times with 100 mL portions of methylene chloride. **Discard the methylene chloride phase.** The aqueous solution contains the herbicides.

11.2.18. Adjust the pH of the solution to $\leq$2 with 1:1 sulfuric acid.

11.2.19. Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

11.2.20. Proceed to section 11.3, Cleanup, if required, or Section 11.4, Extract drying.

11.3. Cleanup

This cleanup step may be necessary if the procedure for determining the herbicide acids only is being followed. (See section 11.2.14) It is not normally required if the acids and esters are being determined. (The usual case.) If cleanup is not required, proceed to section 11.4, Extract drying.

11.3.1. Prepare 45 mL of basic extraction fluid by mixing 30 mL of reagent water with 15 mL of 37% KOH. Use three 15 mL portions of this fluid to partition the extract from section 11.2.12 or 11.2.20, using a small separatory funnel. **Discard the organic phase.**

11.3.2. Adjust the pH of the solution to ≤ 2 with cold (4°C) sulfuric acid. (1:1). Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

11.4. Extract drying

11.4.1. Combine the extracts and pour through a funnel containing acidified sodium sulfate into a flask or bottle containing approximately 10 g acidified sodium sulfate. Rinse the funnel with a little extra diethyl ether.

11.4.2. Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken. Proceed to section 11.5, concentration.

11.5. Concentration

11.5.1. Transfer the ether extract by decanting, or through a funnel plugged with acid washed glass wool, into a Turbovap concentrator tube or a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the flask or bottle with 20-30 mL ether to complete transfer.

11.5.2. Attach a three ball Snyder column to the K-D apparatus, prewet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 2 mL, remove from the water bath and allow to completely cool.

11.5.3. Carefully disassemble the concentrator tube and rinse the lower glass joint with a small amount of diethyl ether.

11.5.4. Add 0.1 mL of methanol.

11.5.5. The extract is now ready for esterification by either the diazomethane solution method (11.6) or the bubbler method (11.7)

11.6. Esterification (diazomethane solution method)

11.6.1. Preparation of Diazomethane solution

- **CAUTION: Diazomethane is potentially explosive.**
- **A temporary shield or the sash of the hood must protect the face and body of the analyst.**
- **Never heat solutions of diazomethane above 90°C, due to the explosive potential.**
- **Do not use glass stirring rods or any glassware with ground glass joints, as this can initiate violent reaction or explosion.**
- **All glassware must be scrupulously cleaned and free from scratches, to avoid potential initiation of violent reaction or explosion.**

11.6.1.1. Weigh out 10.0 g potassium hydroxide in a 125 mL beaker. Add 16 mL water and 20 mL ethanol. Mix well until the potassium hydroxide is dissolved and pour into the reaction vessel.

11.6.1.2. Attach a 100 mL receiving flask to the condenser and cool the receiver in an ice bath.

11.6.1.3. Fill the condenser with dry ice, then add acetone slowly until the cold finger is about one third full.

11.6.1.4. Mix 10.0 g diazald and 90 mL ether. Place in a separatory funnel over the reaction vessel.

11.6.1.5. Warm the reaction vessel on the water bath to 50-60°C or until the ether begins to reflux. CAUTION: Do not allow the temperature to exceed 70°C. Add diazald solution over a period of 40 minutes. The rate of distillation should approximate the rate of addition. Replenish the cold finger with dry ice as necessary.

11.6.1.6. When the diazald solution has been used up, slowly add 10 mL of ether and continue distillation until the distillate is colorless.

11.6.1.7. The diazomethane solution is documented with a lot number. It is stored in a freezer at -10 to -20°C and has an expiration date of six months.

11.6.2. Disposal of outdated diazomethane solutions

11.6.2.1. Add 20 mL of ether to 2 mL of glacial acetic acid in a large beaker in the hood.

11.6.2.2. Add the diazomethane solution slowly to the acetic acid. The yellow color of the diazomethane disappears as it reacts with the acetic acid. If the yellow color persists at any time during the addition, and does not disappear with gentle swirling of the beaker, add additional acetic acid in ether before continuing the diazomethane addition.

11.6.2.3. Dispose of the ether solution in the non-chlorinated wastes bottle.

11.6.3. Esterification (Diazomethane solution method)

11.6.3.1. Add approximately 2 mL of diazomethane solution and let sit for 10-15 minutes.

11.6.3.2. Add approximately 0.2 g of silicic acid to the extract. Allow to spontaneously evaporate to about 1.0 mL, then make up to 10 mL with hexane.

11.6.3.3. Extract is ready for analysis by gas chromatography.

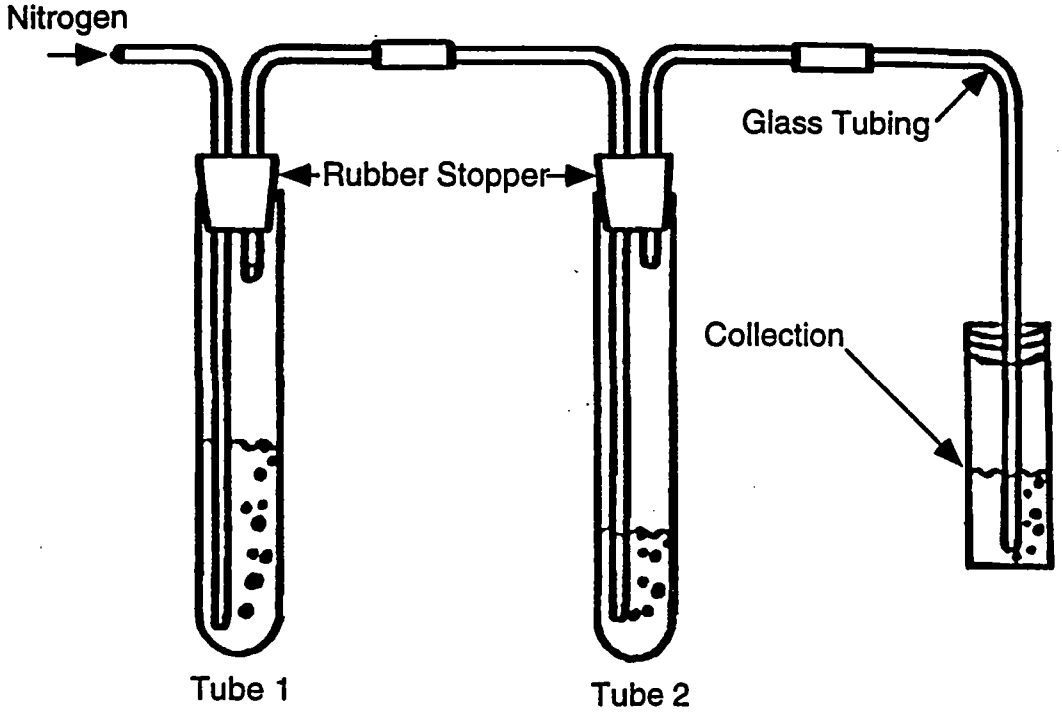
11.7. Esterification (Bubbler Method)

11.7.1. Assemble the diazomethane apparatus (Figure A1) in a hood. Add 10 mL of diethyl ether to tube 1. Add 5 mL of 2% methanolic KOH, 3 mL of ether and 0.5-1 g of diazald to tube 2.

11.7.2. Place the tip of the disposable pipet into the vial containing the first sample extract. Apply nitrogen flow (approx. 10 mL/min) to bubble diazomethane through the sample extract for about 1 minute, or until the yellow color persists. Replace the disposable pipet and place the tip into the vial containing the second extract. Continue until the diazald is consumed. (An additional 0.1-0.5 g diazald may be added to extend the generation of diazomethane).

11.7.3. Allow the extracts to stand for 20 minutes, then add approximately 0.2 g of silicic acid to each extract. Allow to stand for an additional 20 minutes.

11.7.4. Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.



12. DATA ANALYSIS AND CALCULATIONS

Not applicable

13. METHOD PERFORMANCE

Refer to CORP-GC-0001 for details of method performance.

14. POLLUTION PREVENTION

Refer to section 14 of the main body of this SOP.

15. WASTE MANAGEMENT

Refer to section 15 of the main body of this SOP.

16. REFERENCES

16.1. SW846, Test Methods for Evaluating Solid Waste, Third Edition, Update II, September 1994, Chlorinated Herbicides, Method 8151.

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 11.1.2)

17.1.2. The bubbler esterification method uses methanolic KOH in place of the aqueous KOH / carbitol mixture recommended in method 8150B. This has been found to provide a more effective and reliable esterification.

17.2. Modifications from previous revisions

None

17.3. Tables

Table B1
Herbicide Surrogate Spiking Solutions

Analyte Group	Surrogate Spike Solution ID	Volume (mL)
Herbicides	Herbicides SS	1.0

Table B2
Herbicide Matrix Spike and LCS Solutions

Analyte Group	Matrix Spike Solution ID	Volume (mL)
Herbicides	Herbicides MS	1

Table B3
Herbicide Surrogate Spike Components

Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides SS	2,4-DCAA	Methanol	16

[1]The surrogate is spiked as the free acid

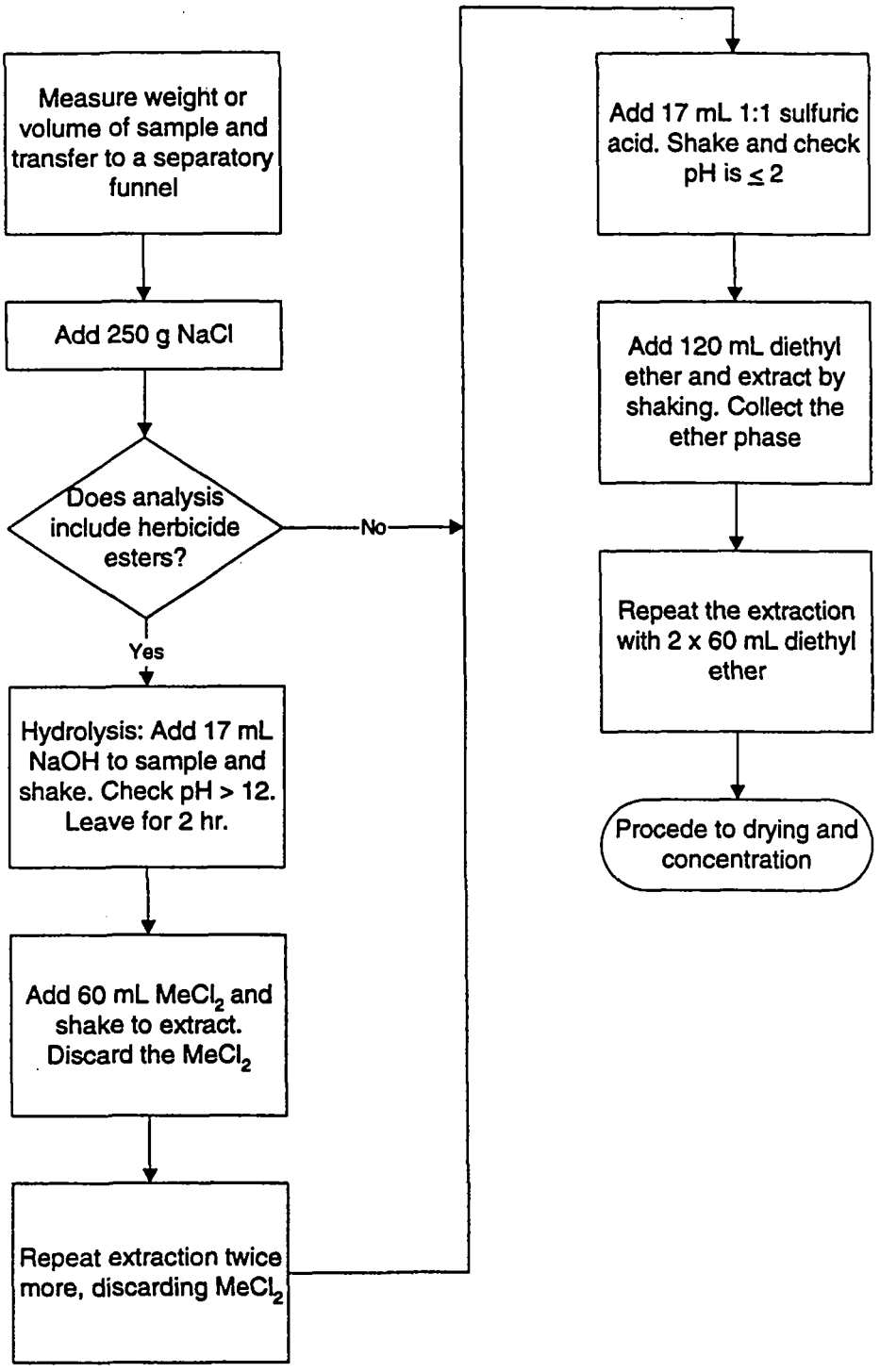
Table B4

Herbicide Matrix Spike Components

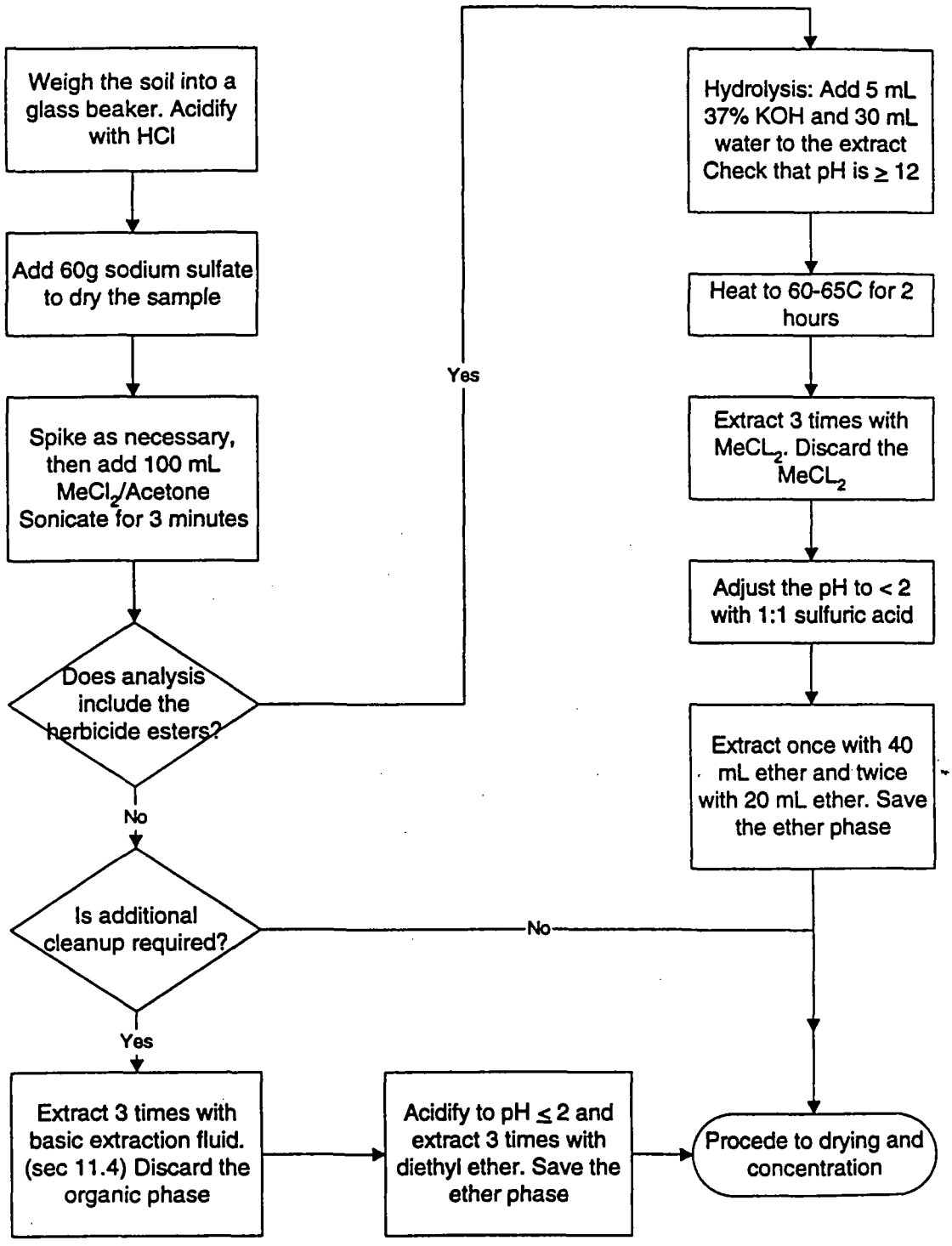
Type	Compounds[1]	Solvent	Conc. (ug/mL)
Herbicides MS	2,4-D	Methanol	16
	2,4-DB		16
	2,4,5-TP (Silvex)		4
	Dalapon		8
	2,4,5-T		4

[1]The herbicide spiking solution contains the herbicides as the free acids.

Extraction of Aqueous Samples



Extraction of Soils and Sediments



Drying, Concentration and Esterification